SAND2019-10762C

Gas-Phase Reactions of Carbonyl Oxides

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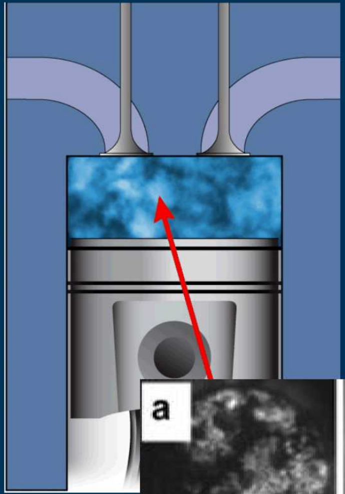
2019 Gordon Conference on Physical Organic Chemistry

Holderness NH

Complex chemical systems

Autoignition chemistry

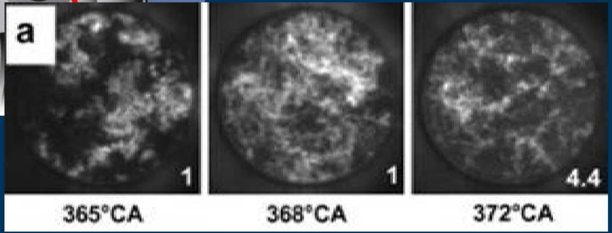


Complex networks of chemical reactions

Deliberate control of reaction conditions

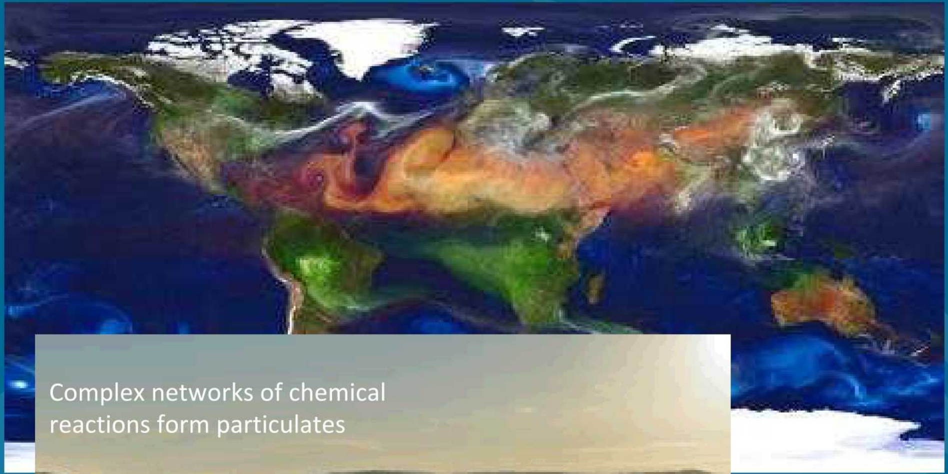
Simple goal: clean/efficient

John Dec, Sandia



Tropospheric oxidation

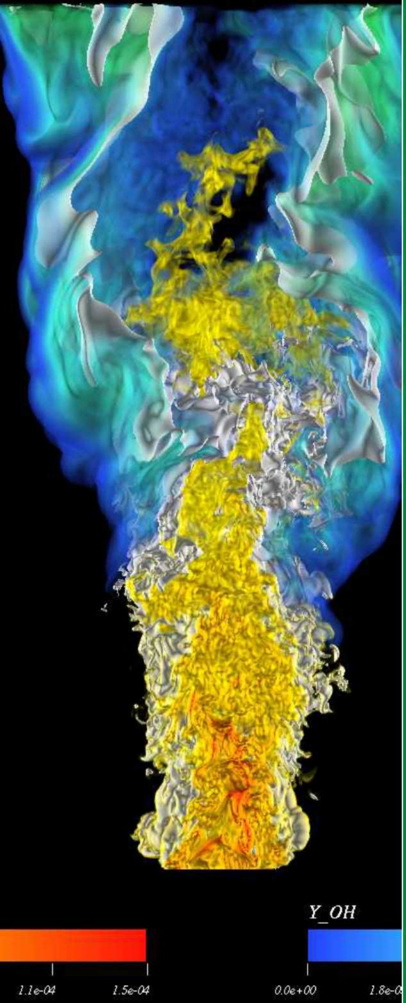
William Putman, NASA/Goddard



Complex networks of chemical reactions form particulates

Human effects on reaction conditions are accidental

What are the “goals”?



Many complex chemical systems depend on a few key reactions – e.g., radical chain branching reactions for autoignition:

$R + O_2 \rightarrow ROO \rightarrow QOOH \text{–}(+O_2)\rightarrow OOQOOH$

$OOQOOH \rightarrow OH + \text{ketohydroperoxide} \rightarrow OH + OH + RO$

Reactions often have multiple possible channels that have different impacts on the complex system behavior

Characterizing individual crucial intermediate steps is often difficult if one looks only at the global system, or even at multistep processes

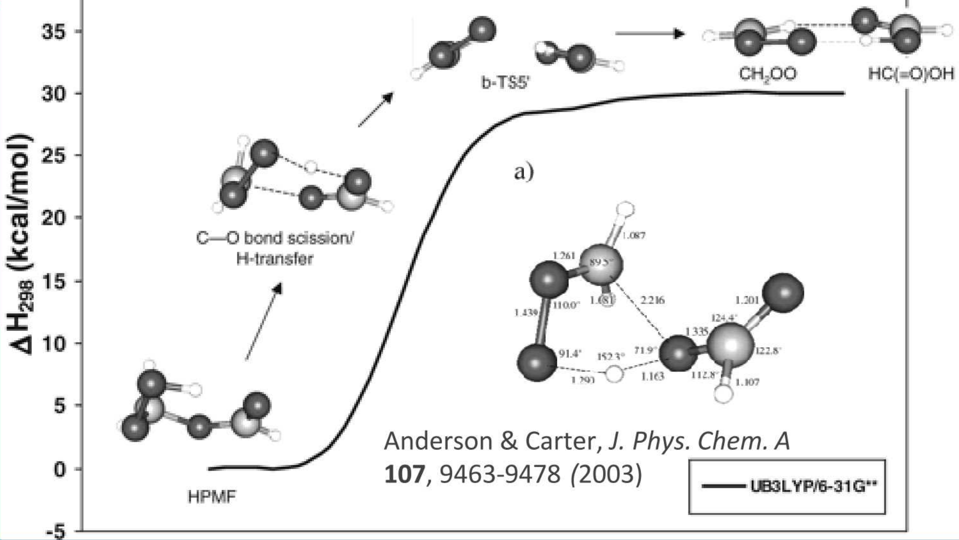
Why carbonyl oxides?

Fundamentally interesting – unusual electronic structure

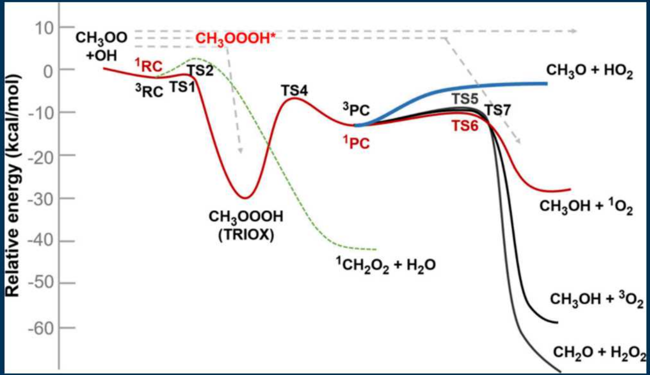
Appear as possible products in oxidation systems

- Dimethyl ether autoignition
- ROO + OH reactions
- Ozonolysis

Information on carbonyl oxide reactivity had been indirect



Anderson & Carter, *J. Phys. Chem. A* **107**, 9463-9478 *(*2003)



Feng Zhang, Can Huang;
J. Phys. Chem. Lett.
DOI: 10.1021/acs.jpclett.9b00781

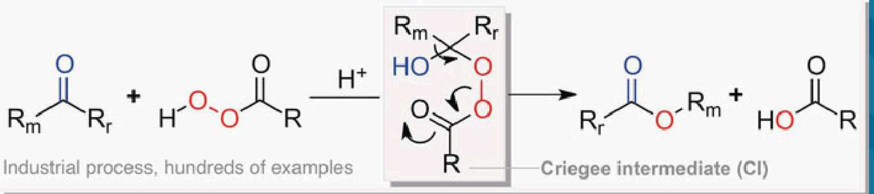
Criegee mechanism for ozonolysis

Three steps

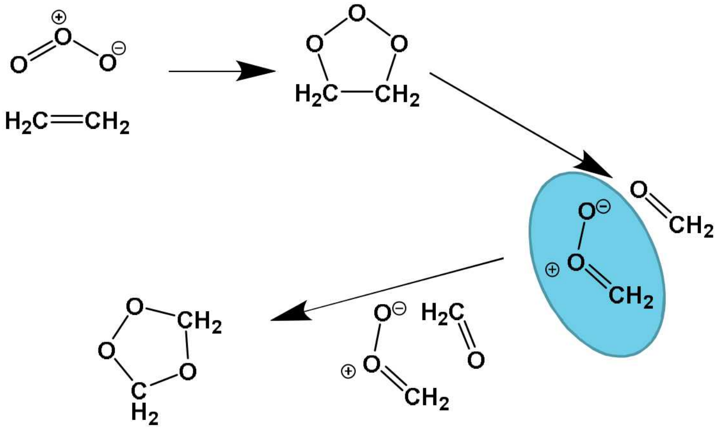
- Cycloaddition of ozone to C=C
- Dissociation to carbonyl and carbonyl oxide “Criegee intermediate”

Not this Criegee intermediate –

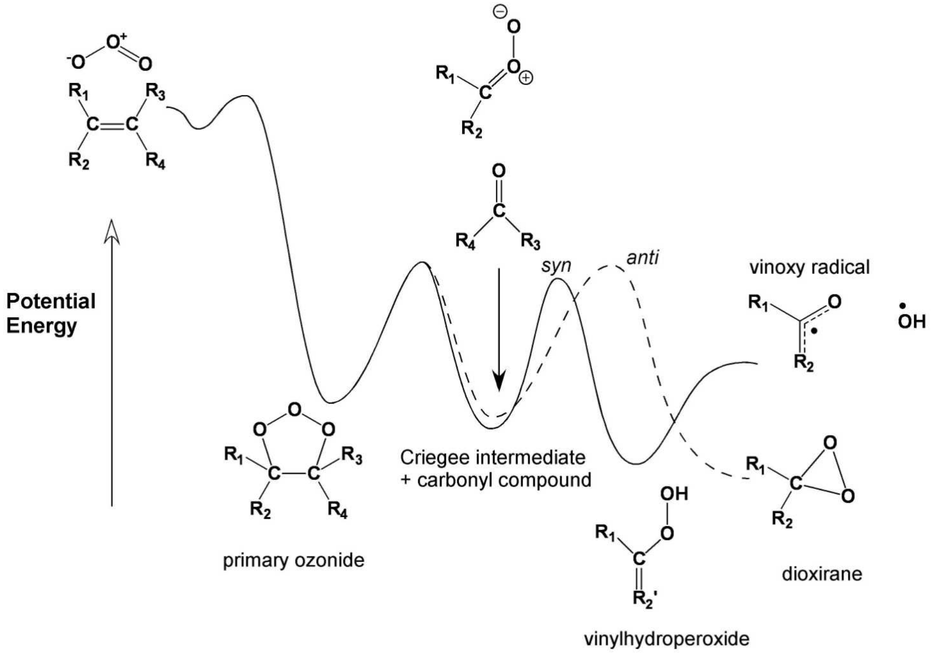
Baeyer-Villiger Reaction



Vil‘ et al., Angew. Chem. Int. Ed. 2018, 57, 3372 –3376

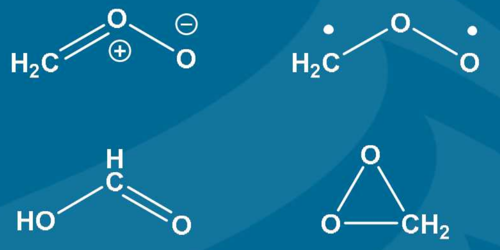


Carbonyl oxides can also undergo other reactions



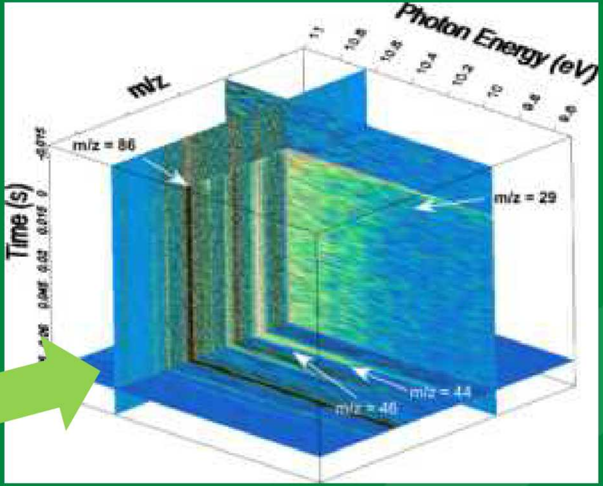
Carbonyl oxides formed in ozonolysis are potential tropospheric reactants

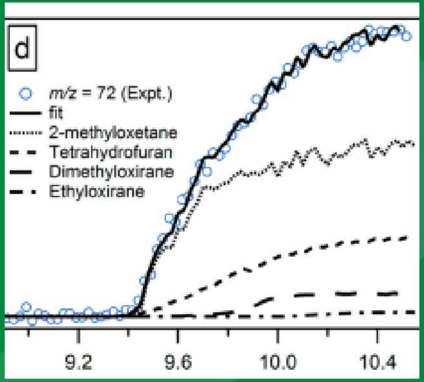
These intermediates are isomers of other more common species



Need a method to specifically detect these isomers

Synchrotron photoionization mass spectrometry can specifically detect and characterize isomeric intermediates





David Osborn

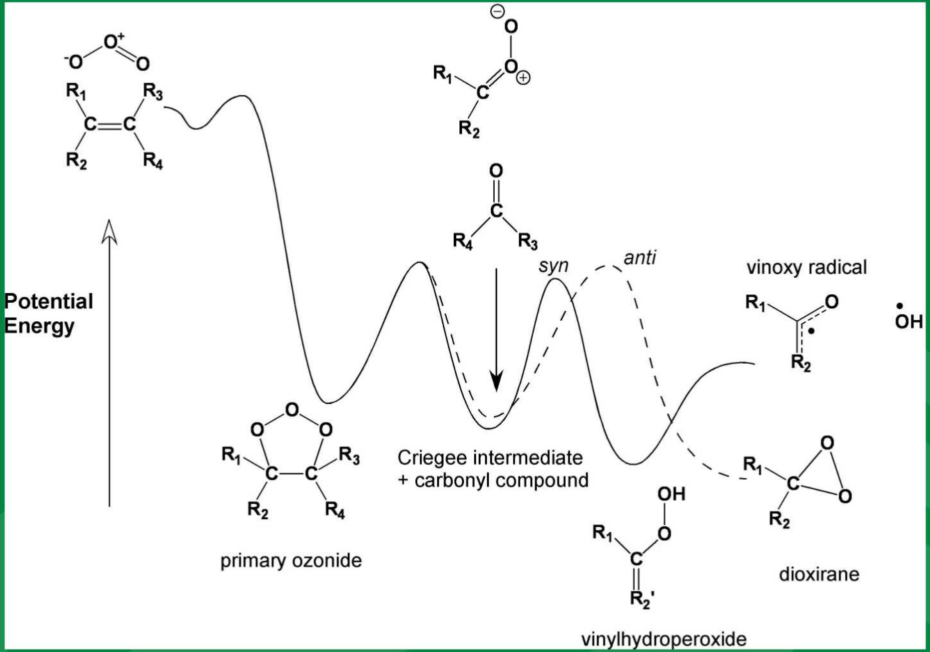
Isomer-Resolved Species Identification

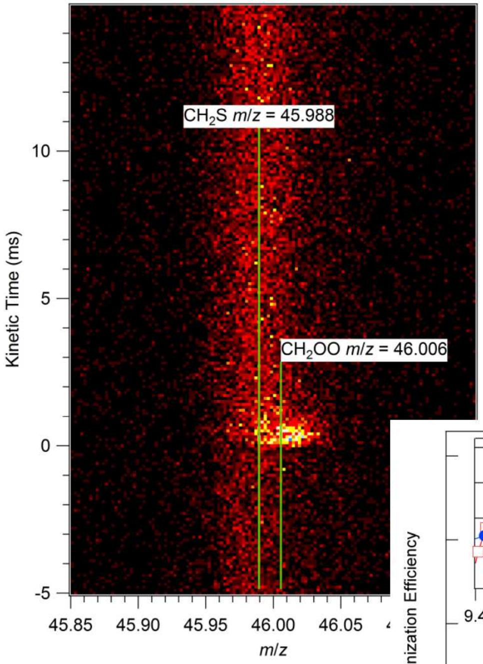
Time-Dependent Chemical Kinetics

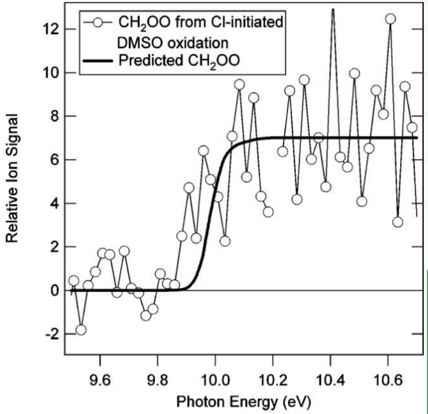
Of course, we need to **make** the intermediates before we can detect them

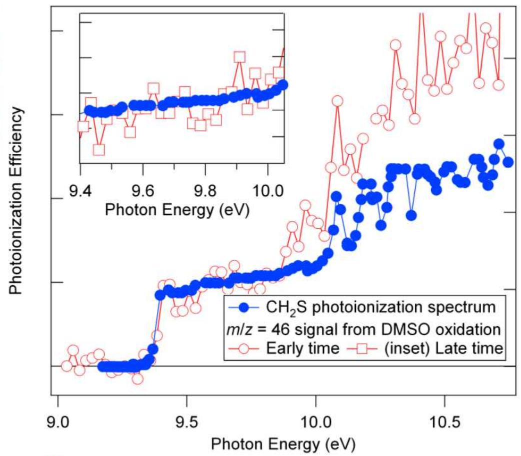
Problem with ozonolysis: reactions is slow **and** exothermic

Reaction proceeds slowly and products disappear rapidly









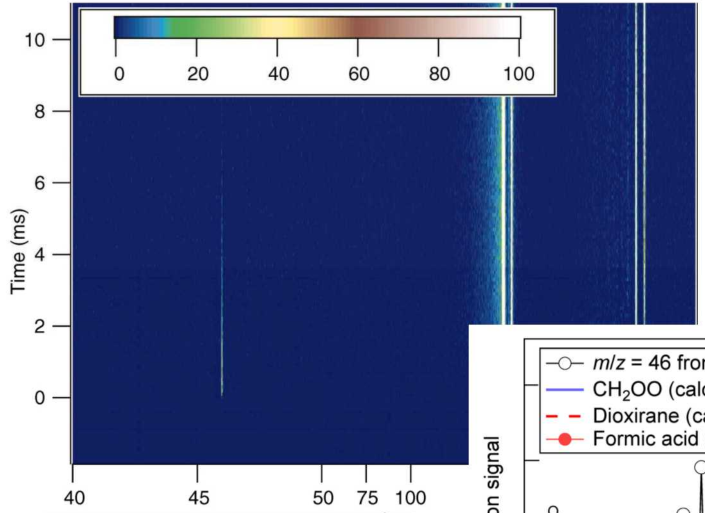
CAT et al., *JACS* **130,** 11883 (2008)

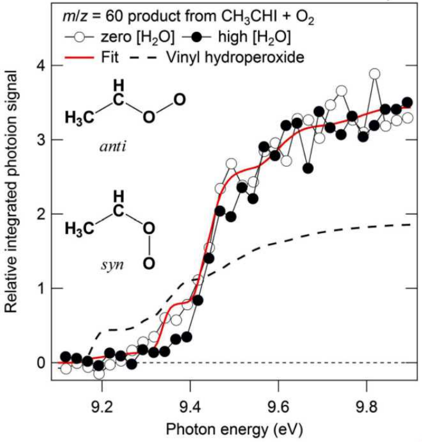
For carbonyl oxides we need to have strategy for direct synthesis

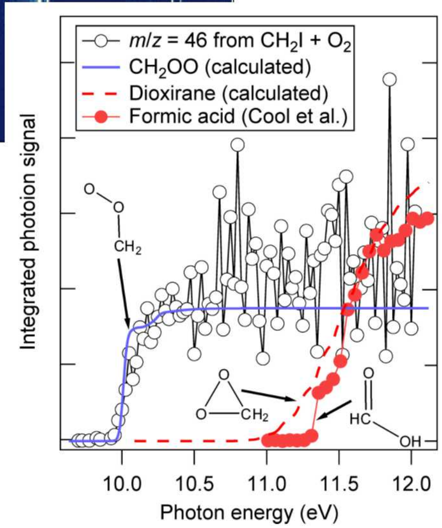
Verify by mass, kinetics, and spectrum

Reaction of CH_3SOCH_2 with O_2 makes CH_2OO

For carbonyl oxides we need to have strategy for direct synthesis





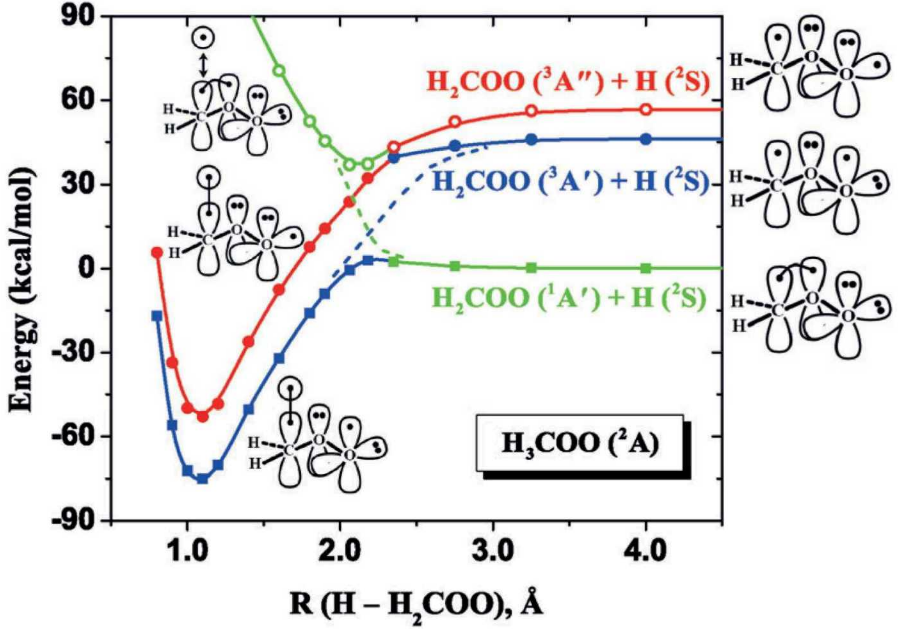


Welz et al., *Science* **335**, 204 – 207 (2012);
CAT et al. *Science* **340**, 177–180 (2013)

- Verify by mass, kinetics, and spectrum
- Reaction of CH_3SOCH_2 with O_2 makes CH_2OO
- Reactions of gem-iodoalkyl radicals with O_2 make lots of carbonyl oxides

- UV, IR, and microwave spectra for carbonyl oxides have been measured
- Many groups now measure carbonyl oxide reaction kinetics directly

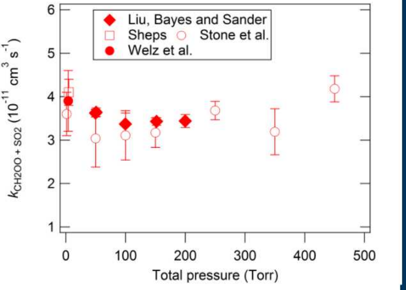
Craig Murray (Irvine); Marsha Lester (Penn); Jim Lin (IAMS); Andrew Orr-Ewing (Bristol); Bill Green (MIT); Paul Seakins, Dan Stone (Leeds), etc.

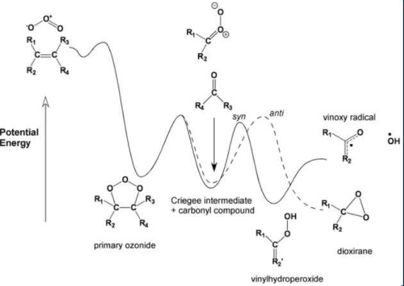


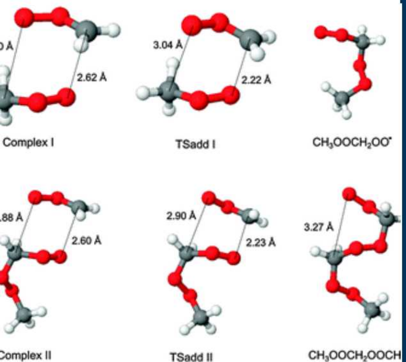
Miliordos and Xantheas, *Angew. Chem. Int. Ed.* **55**, 1015-1019, 2015

- Carbonyl oxides have multireference electronic character
  - Ground state is dominantly the closed-shell singlet zwitterion

  - How should they react? … not like radicals!
  - CH_3OO + NO $\quad$ 7.5×10^{-12} $cm^3\ s^{-1}$
    Lightfoot et al., *Atmos. Environ. A* **26**, 1805 – 1961 (1992)
  - CH_2OO + NO $\quad$ $< 6 \times 10^{-14}$ cm^3 s-1
    Welz et al., *Science* **335**, 204 – 207 (2012)
  - Nevertheless, carbonyl oxides undergo rapid reactions with some other closed-shell species





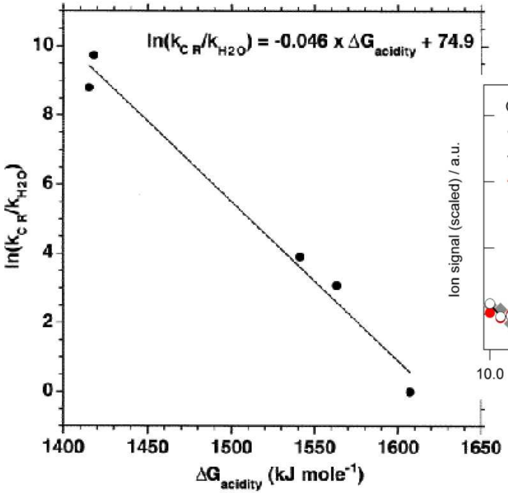


The chemistry of ozonolysis was largely worked out from solution phase – gas phase can be different!

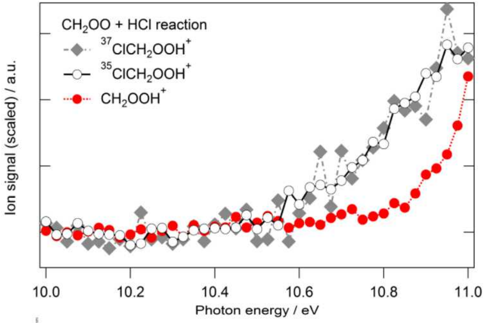
Criegee (1975) outlined four types of reactions that carbonyl oxides undergo: dimerization, reaction with carbonyls, isomerization, and reactions with "proton active substances"

Generalization (CAT, *Annu. Rev. Phys. Chem.* 2017):

- Reactions with other 1,3 bipoles
- Cycloadditions
- Unimolecular reactions
- Insertions
- Addition to radical species



Tobias and Ziemann, *J. Phys. Chem. A* (2001) **105**, 6129-6135



Caravan, Rotavera, CAT et al., unpublished

Direct kinetics measurements now exist for all types of carbonyl oxide reactions

- Reactions with other 1,3 bipoles
- Cycloadditions
- Unimolecular reactions
- **Insertions**
- Addition to radical species

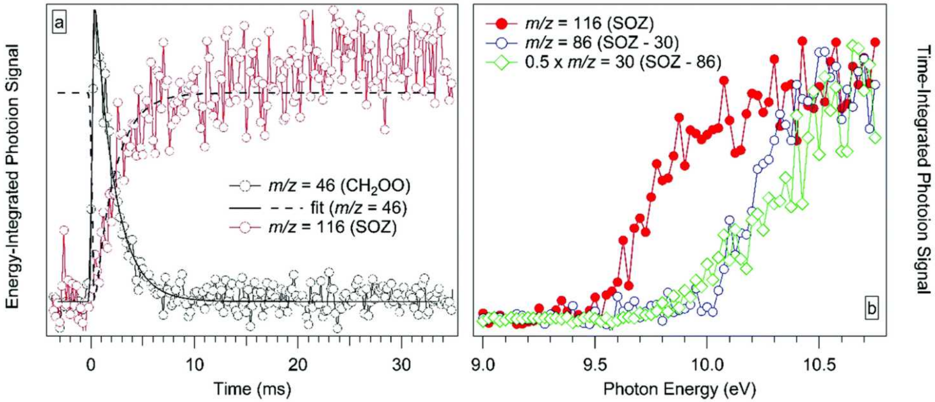
Carbonyl oxide reactions in solution: ROH>H_2O>CH_3CO_2H

In gas phase RCO_2H >> ROH, H_2O

Fast ("supercollisional") reaction general for all acids

(Welz et al., *Angew. Chem. Int. Ed.* 53, 4547-4550 (2014); Foreman et al., *Angew. Chem. Int. Ed.* 55, 10419-10422 (2016); Chhantyal-Pun et al., *Angew. Chem. Int. Ed.* 56, 9044-9047 (2017); CAT et al, *Environ. Sci. Technol.* **53**, 1245-1251 (2019))

Insertion into acid, as in solution CH_2OO + HCl → $ClCH_2OOH$ (c.f. Turner and Gäb, *J. Org. Chem.* **1992** *57*, 1610-1613)



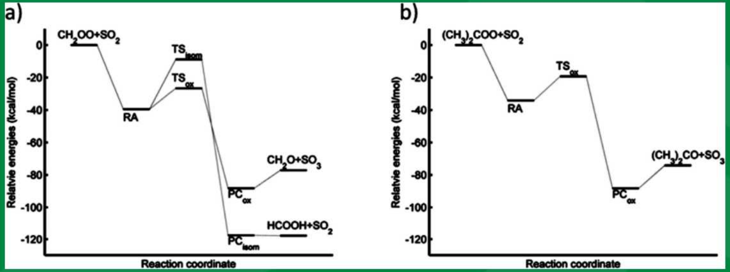
Eskola, CAT et al. *Phys. Chem. Chem. Phys.*, 2018, **20**, 19373-19381

Direct kinetics measurements now exist for all types of carbonyl oxide reactions

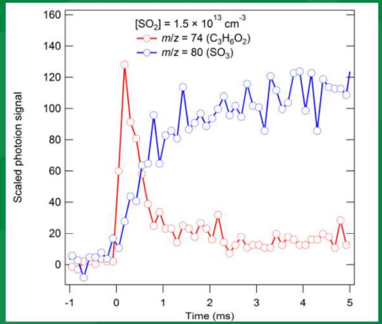
- Reactions with other 1,3 bipoles
- **Cycloadditions**
- Unimolecular reactions
- Insertions
- Addition to radical species

Cycloaddition to carbonyls forms secondary ozonides

Reactions that transfer O atom (e.g. to SO_2) can be mediated by cycloaddition



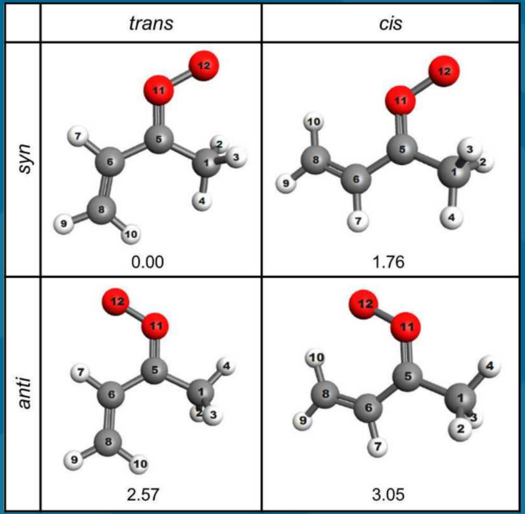
Kurtén et al., *J. Phys. Chem. A* **115**, 8669–8681 (2011)



CAT et al. *Science* **340**, 177–180 (2013)

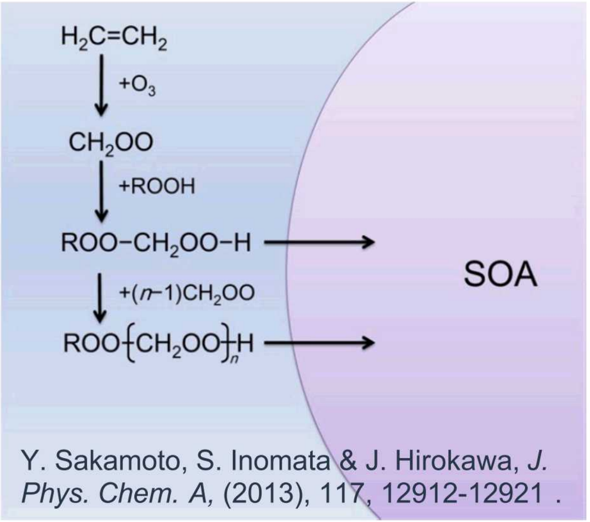
Reactions of a "conjugated" carbonyl oxide

Methyl vinyl ketone oxide, product in isoprene ozonolysis

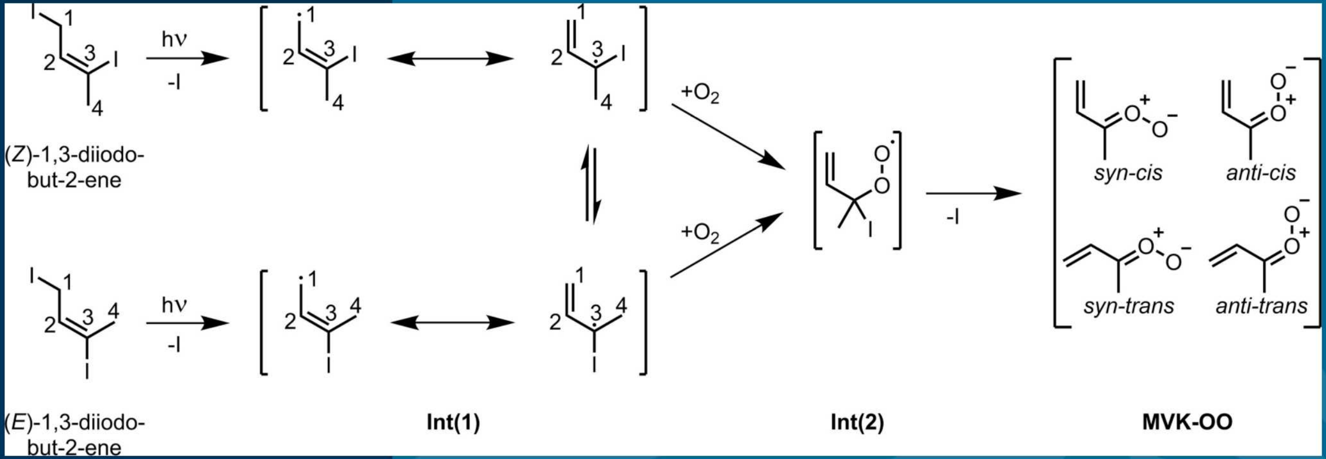


Barber et al., *J. Am. Chem. Soc.* (2018), 140, 10866-10880

"Oligomerization" reactions of carbonyl oxides and formation of highly oxygenated compounds



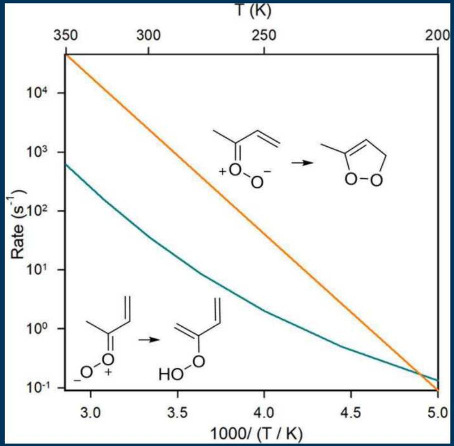
Conjugated carbonyl oxides from isoprene ozonolysis



Does C=C bond affect reactivity? Lester group (Penn) discovered way to make MVK-OO

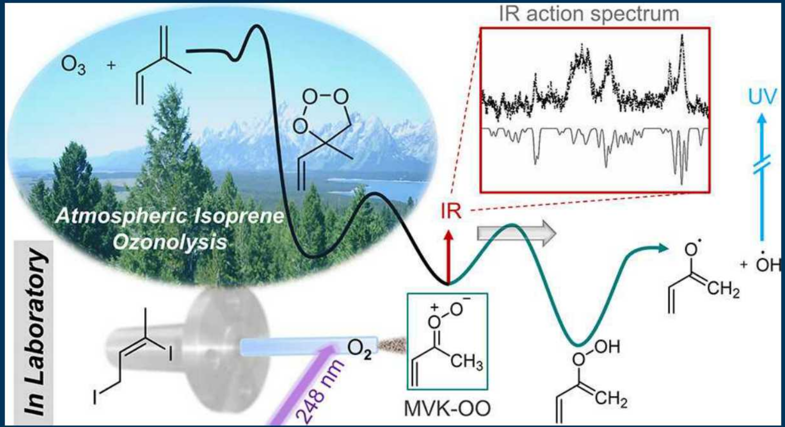
Barber et al., *J. Am. Chem. Soc.* (2018), 140, 10866-10880

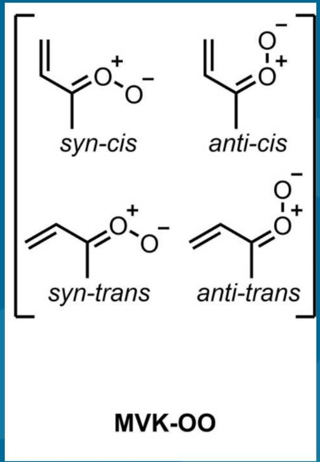
Conjugated carbonyl oxides from isoprene ozonolysis



Dramatic difference in unimolecular decay predicted between *syn* and *anti* conformers

Molecular beam experiments give "action" spectrum

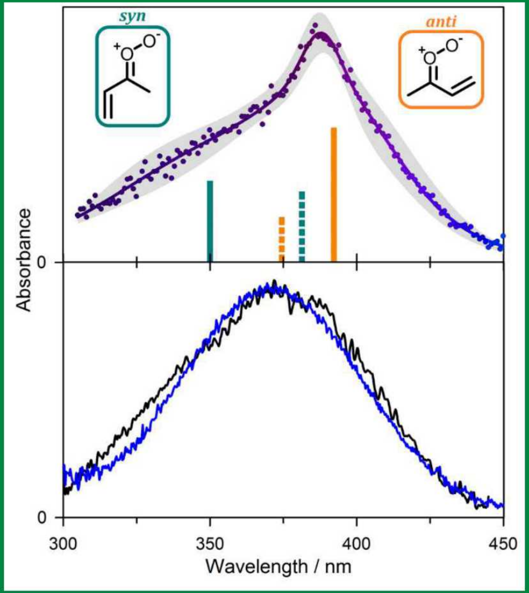




Does C=C bond affect reactivity? Lester group (Penn) discovered way to make MVK-OO

Barber et al., *J. Am. Chem. Soc.* (2018), 140, 10866-10880

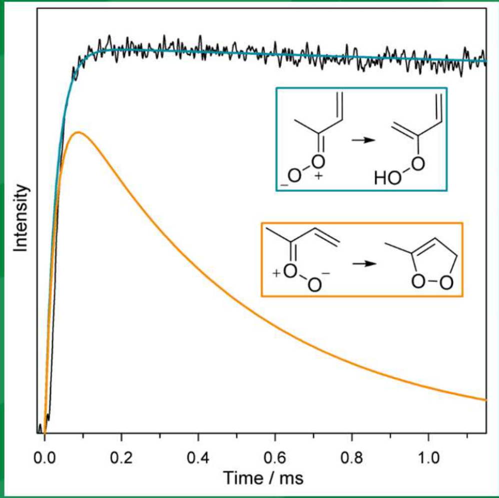
Can measure thermal kinetics of MVK-OO with same source



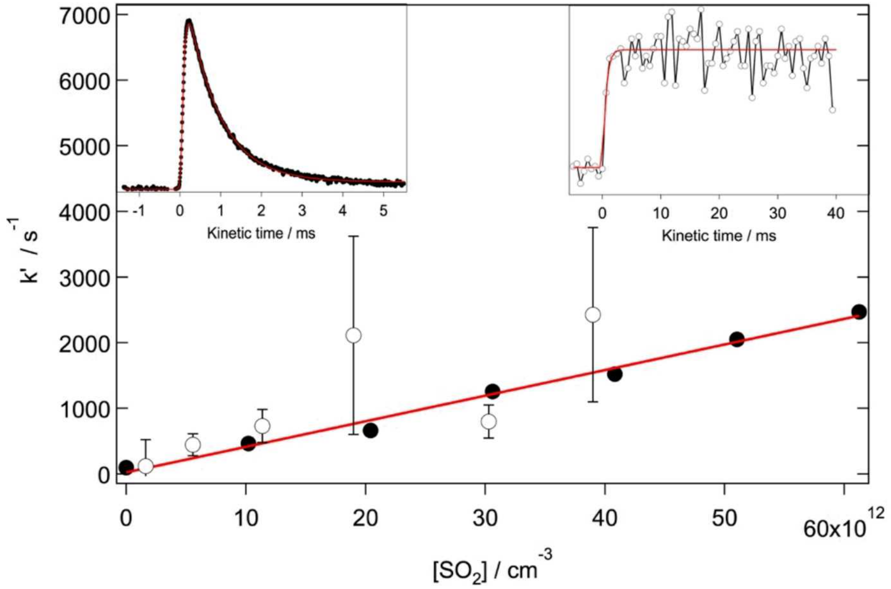
Broadband time-resolved absorption (Sheps)
Absorption differs from action spectrum

Lenny Sheps

“Zero-reagent” decay suggests only *syn*-conformers survive long enough to measure bimolecular kinetics



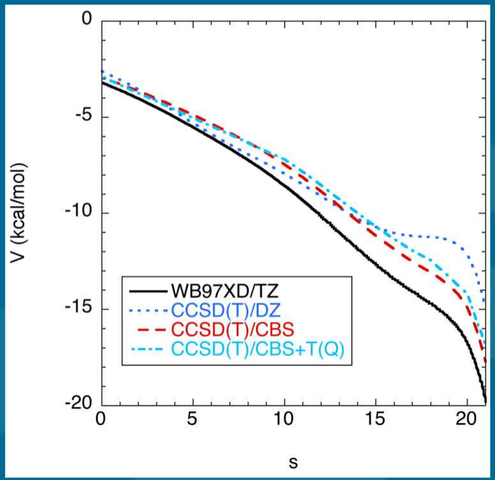
Sheps, Caravan, Lester, Klippenstein, CAT et al., unpublished



Reaction with SO_2 has rate coefficient $(3.9 \pm 0.5) \times 10^{-11}$ cm^3 s^{-1}) similar to small carbonyl oxides

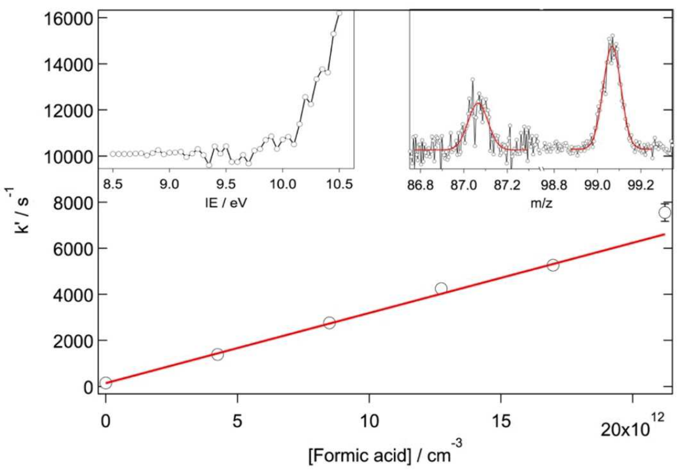
SO_3 is observed as a product

Calculation for SO_2 reaction shows a saddle point in the entrance channel



Search for SOZ unsuccessful

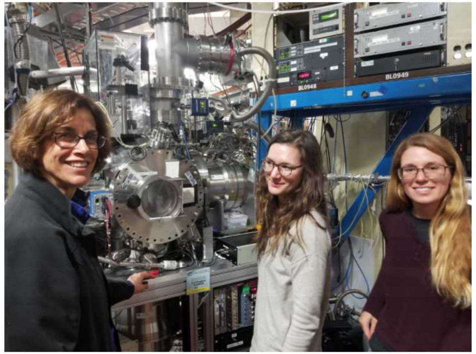
Sheps, Caravan, Lester, Klippenstein, CAT et al., unpublished



Reaction with formic acid is rapid, k = (3.0 ± 0.1) × 10^{-10} cm^3 s^{-1}, and calculated barrierless

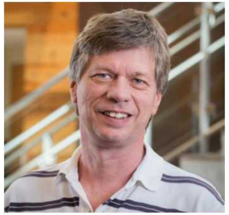
Product is observed at fragment ions characteristic of hydroperoxy ester insertion products

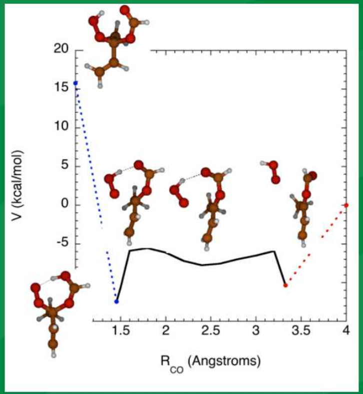
Reaction with water is too slow to measure – MVK oxide can reach relatively high steady state



Marsha Lester, (Mike Vansco), Rebecca Caravan, Kristen Zurasky

Stephen Klippenstein





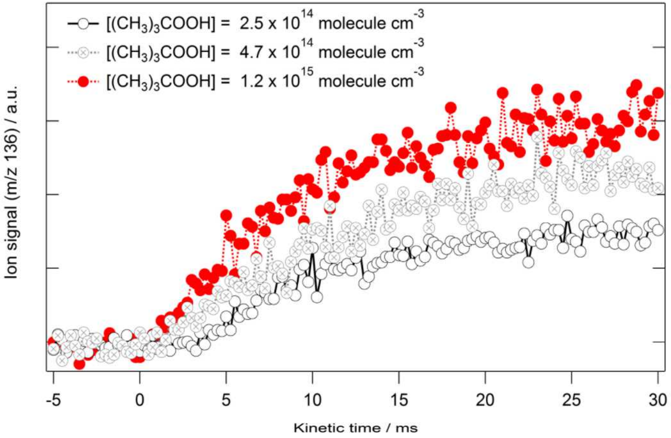
Sheps, Caravan, Lester, Klippenstein, CAT et al., unpublished

Do other “proton-active” species in the gas phase also insert?

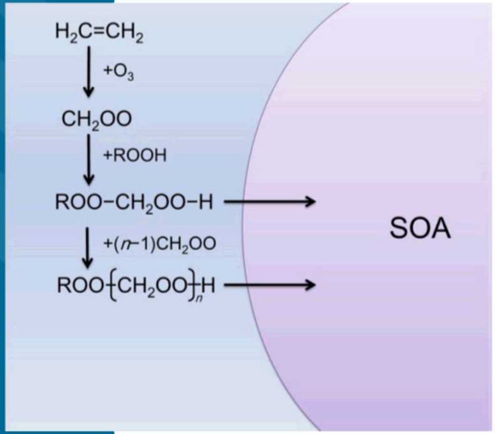
ROOH – CH_2OO reaction with $(CH_3)_3COOH$ makes adduct

Insertion product retains an OOH group, can undergo reaction with another carbonyl oxide

How long could this go on?



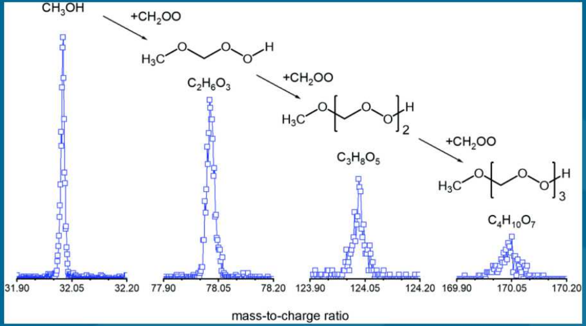
Caravan, CAT et al., unpublished

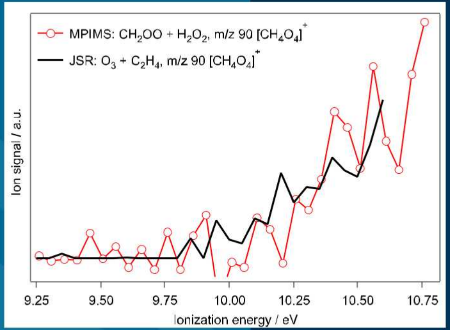


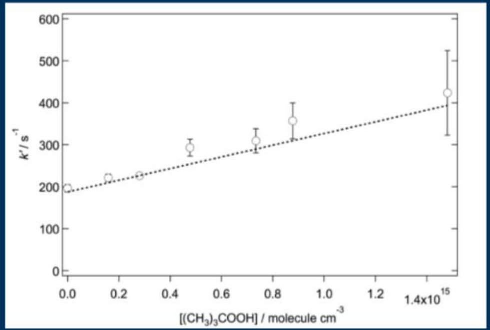
Sakamoto et al., *J. Phys. Chem. A*, (2013), 117, 12912-12921 .

Long reaction sequences are observed in ozonolysis (Rousso et al., *Phys. Chem. Chem. Phys.*, 2019, **21**, 7341-7357)

Theoretical kinetics compared to experiment for specific reactions





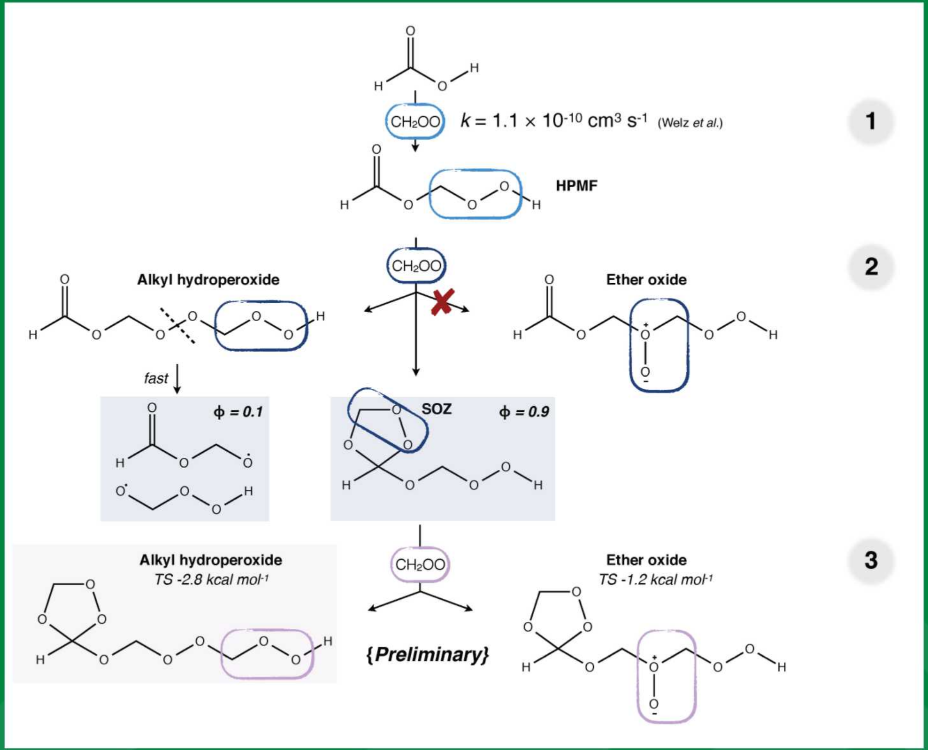


Photoionization spectra from ozonolysis can be compared to photolytic “direct” kinetics

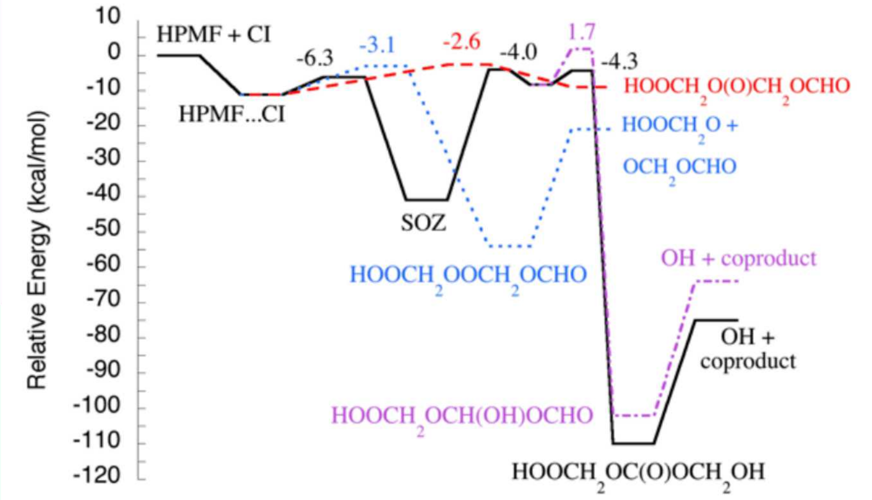
Nils Hansen

Validated theory to calculate rate coefficients that aren’t measured

Combine to give a full model



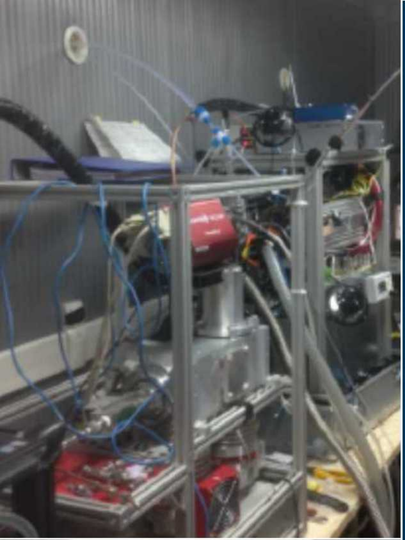
Sequence of reactions starting from reaction with formic acid maintains –OOH

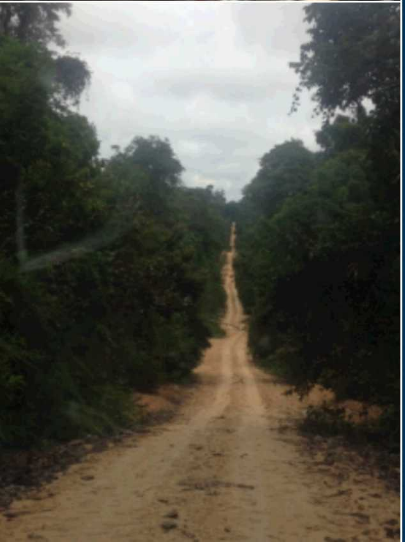


Confirms and quantifies previous proposals inferred from laboratory ozonolysis measurements

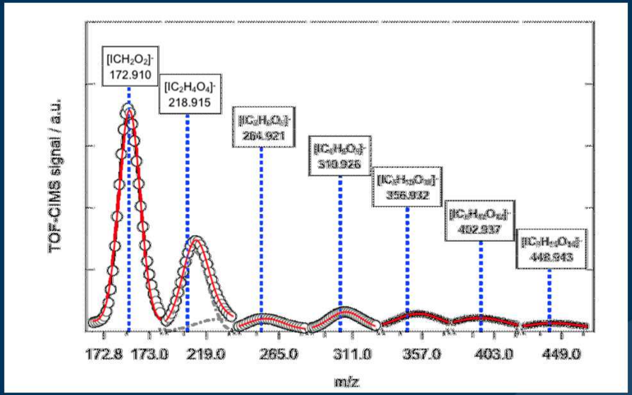
Some unexpected predictions – stabilized hydroperoxy-SOZ product

These sequences have never been confirmed to produce aerosol in the field

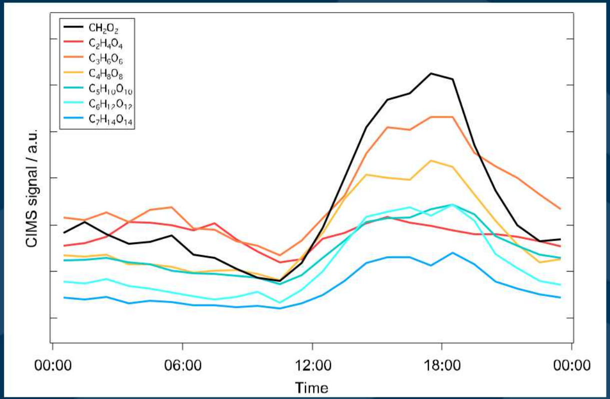




CIMS measurements of aerosol and gas phase in Brazil



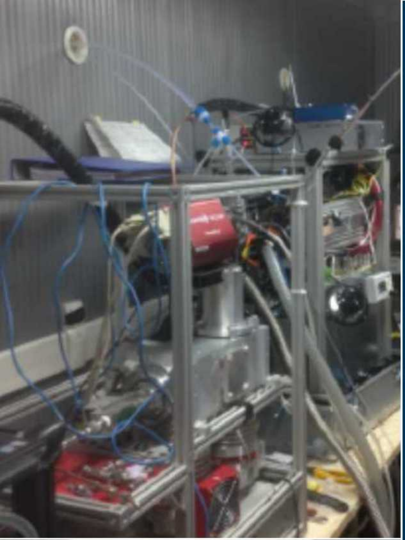
Sequences of CH_2OO addition

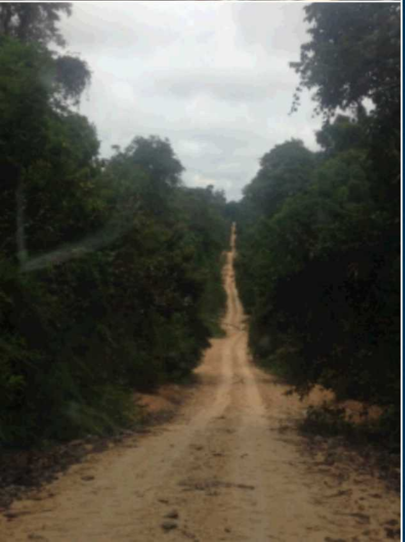


Diurnal profiles suggest a common origin

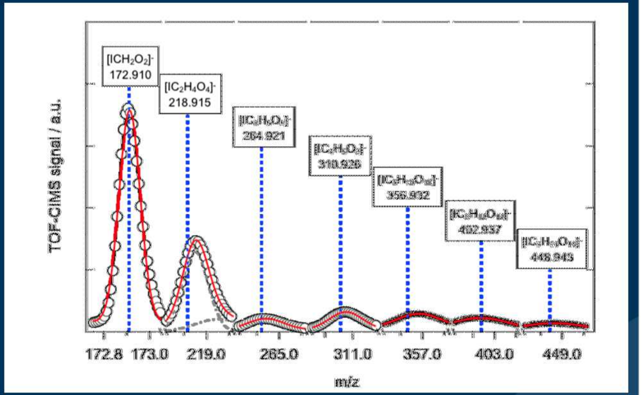
← Carl Percival, Tom Bannan et al.

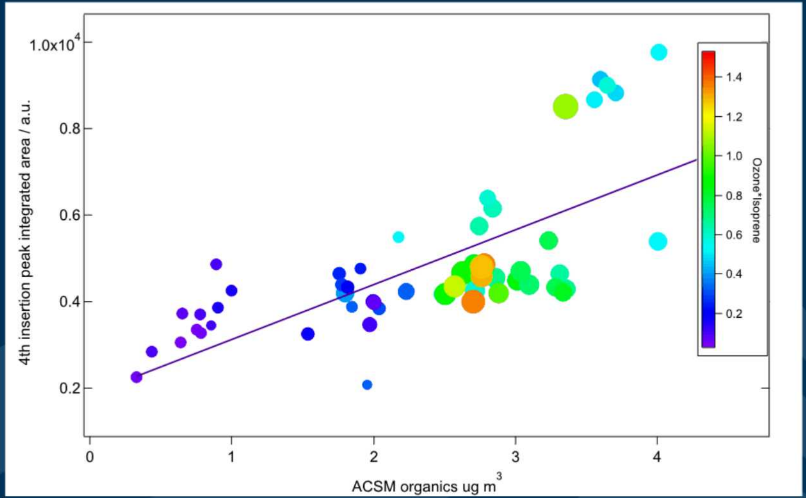
These sequences have never been confirmed to produce aerosol in the field





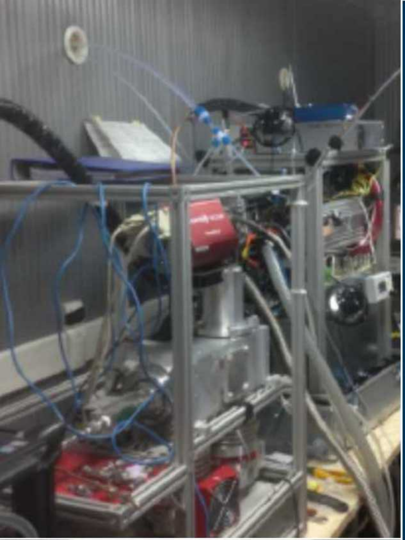
CIMS measurements of aerosol and gas phase in Brazil

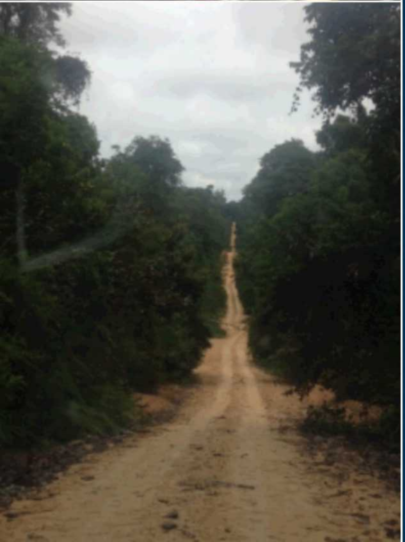




Correlated in gas phase and aerosol phase

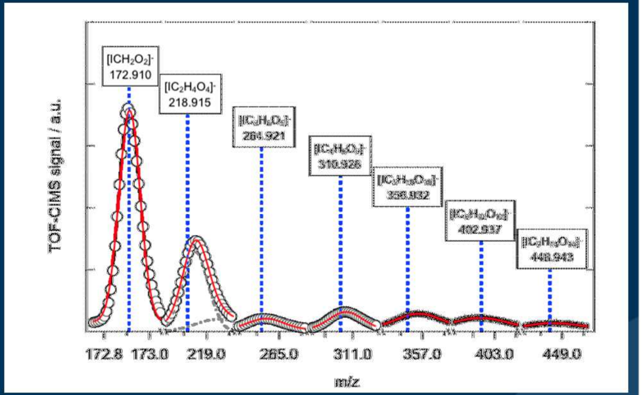
← Carl Percival,
Tom Bannan et al.

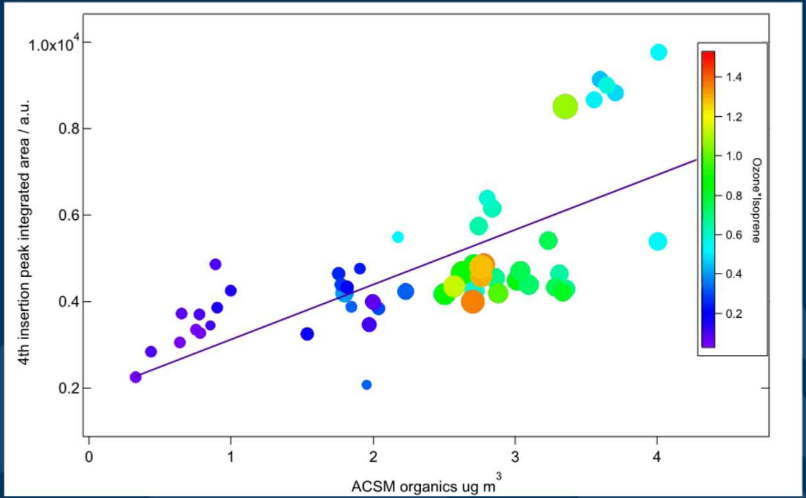




These sequences do appear to produce aerosol in the Amazon forest

CIMS measurements of aerosol and gas phase in Brazil





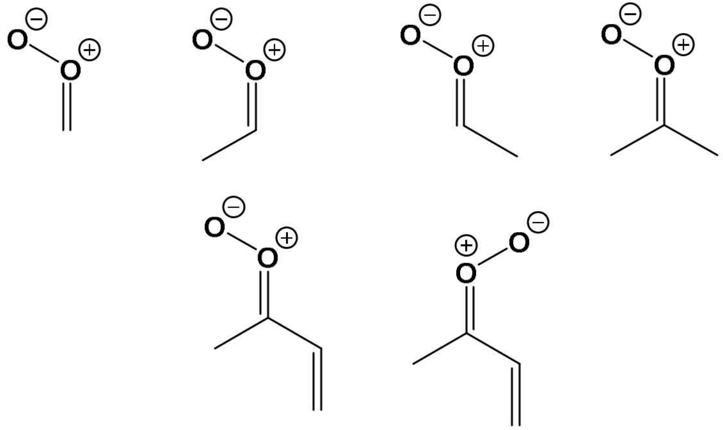
Correlated in gas phase and aerosol phase

← Carl Percival,
Tom Bannan et al.

Many gas phase carbonyl oxides have been produced and characterized

Reaction rate coefficients and product branching fractions have been measured for unimolecular and bimolecular reactions

Direct kinetics measurements are changing models of complex chemical systems like secondary aerosol formation



Carbonyl Oxide Research in the CRF Combustion Chemistry Department

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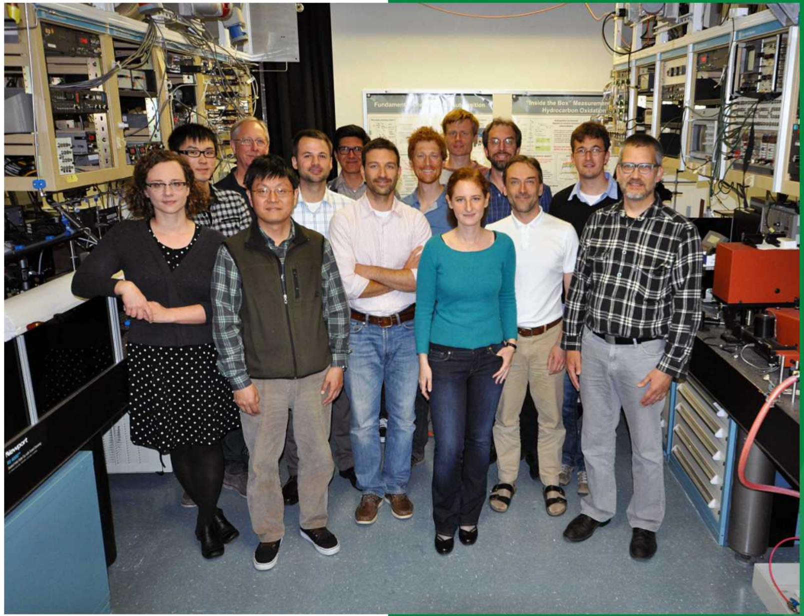

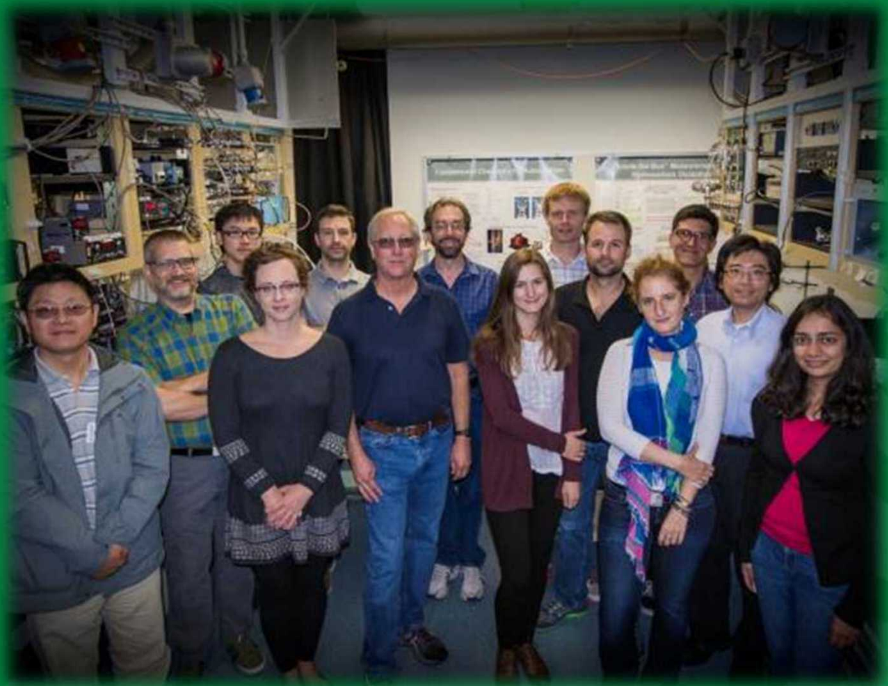

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